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QUANTUM LATTICE FLUCTUTATIONS IN A 1-DIMENSIONAL CHARGE-DENSITY-WAVE MATERIAL: LUMINESCENCE AND RESONANCE RAMAN STUDIES OF AN MX SOLID

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Quantum Lattice Fluctuations in a 1-Dimensional Charge-Density-Wave Material: Luminescence and Resonance Raman Studies of an MX Solid

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ABSTRACT

Luminescence spectra, both emission and excitation, and the excitation dependence of the resonance Raman (RR) spectra have been measured for a 1-dimensional charge-density-wave solid, $[Pt(L)_2Cl_2][Pt(L)_2](ClO_4)_4$; L=1, 2-diaminoethane. The luminescence experiments support the existence of tail states in the band gap region, which indicate the presence of disorder. In contrast, the RR measurements conclusively demonstrate that the effects of static structural disorder on the vibrational spectroscopy can be neglected. This apparently paradoxical result can be explained by considering the zero-point motion of the lattice. Our experimental results are compared to recent theoretical models.

1. INTRODUCTION

It has been known for some time that the zero-point motion in *trans*-polyacetylene (PA) is comparable to the Peierls distortion.[1] In a recent paper, this has been pointed out to be true for a wide range of electronically 1-dimensional (1-D) solids.[2] McKenzie and Wilkins have considered the effect of lattice fluctuations on the density of states in the gap region in terms of a modulation of the band gap and the associated disorder. They found that within the Born-Oppenheimer approximation zero-point and thermal lattice motion can be treated as a static random potential that will produce a finite density of electronic states in the energy gap region. McKenzie and Wilkins derived an analytical expression for the density-of-states in the gap region. Experimentally, this will be manifested as an absorption tail that extends into the gap region. Such effects have also been qualitatively predicted by others using semiclassical Monte Carlo techniques.[3] While band tail absorption is observed in PA [4] and other 1-D materials, it is generally difficult to definitively rule out static disorder (i. e. ordinary inhomogeneous broadening) as an origin for the tail states. Resonance Raman (RR) studies have established the presence of static structural disorder in PA, making inhomogeneous broadening a strong candidate for the origin of the tail states observed in this material.[5] We present here the results of optical studies on a 1-D metal-halogen-mixed-valence (MX) solid — $[Pt(L)_2][Pt(L)_2Cl_2](ClO_4)_4$; L=1, 2-diaminoethane, (hereafter abbreviated "PtCl"). The results enable us to establish that static disorder has negligible effects on the

electronic states for this material. The results are in accord with the possibility that the observed band tail states result from lattice fluctuations.

The MX class of materials are 1-D crystalline solids composed of chains of alternating transition metal and halide ions.[6] These systems typically display a commensurate charge density wave (CDW) on the metal ions, accompanied by a Peierls distortion of the halide sub lattice, and are of particular interest for the extreme tunability (chemically and structurally) of their e-e and e-phonon couplings and thus CDW strengths. They have been successfully modeled using a 3/4-filled, 2-band Peierls Hubbard Hamiltonian which bears intriguing similarities to those appropriate for other electronically low-dimensional solids including the high-T_c oxide superconductors.[7] For these reasons, these materials have been the subject of significant experimental investigation.[8-20]

The strength of the CDW can be electronically controlled by varying the bridging halide and the metal ion and can be structurally controlled by the choice of ligands and counterions.[9,10,11] A three-dimensional template is formed by the ligand group and the counterion which controls the structure of the soft MX chain axis. By varying the ligand or the counter ion the strength of the CDW can be tuned through systematic variation of the Pt--Pt spacing along the chain axis.[11] We have employed this structural template effect to correlate various measures of CDW strength (the Raman chain mode frequency, the band edge, the Pt--Pt separation, and the ratio of short to long Pt-X bond lengths).

2. EXPERIMENTAL

The crystals were grown using previously published methods.[10] The luminescence spectra were collected with a SPEX flourimeter outfitted with an IR sensitive PMT and gratings blazed for 1000 nm. The data has been corrected for the spectral response of the PMT. Raman measurements were performed using Ti:sapphire, HeNe and Ar^+ lasers and previously described CCD array and PMT detection schemes.[18] To avoid laser heating of the sample, laser power was lowered until no heating effects were observed in the Raman spectra.

3. RESULTS AND DISCUSSION

The luminescence excitation spectra shows a dramatic temperature dependence, Fig. 1. The luminescence excitation edge broadens significantly, as the temperature is increased. Furthermore, even at low temperatures, a tail is observed in the excitation profile for energies lower than approximately 2.36 eV or 525 nm. Direct absorption measurements in the band tail region show a similar temperature dependence.[16] For a static 1-dimensional lattice, one would expect an inverse square root divergence of the absorption above and no absorption below the band edge. It is reasonable to conclude that the band edge is smeared out by some kind of disorder.
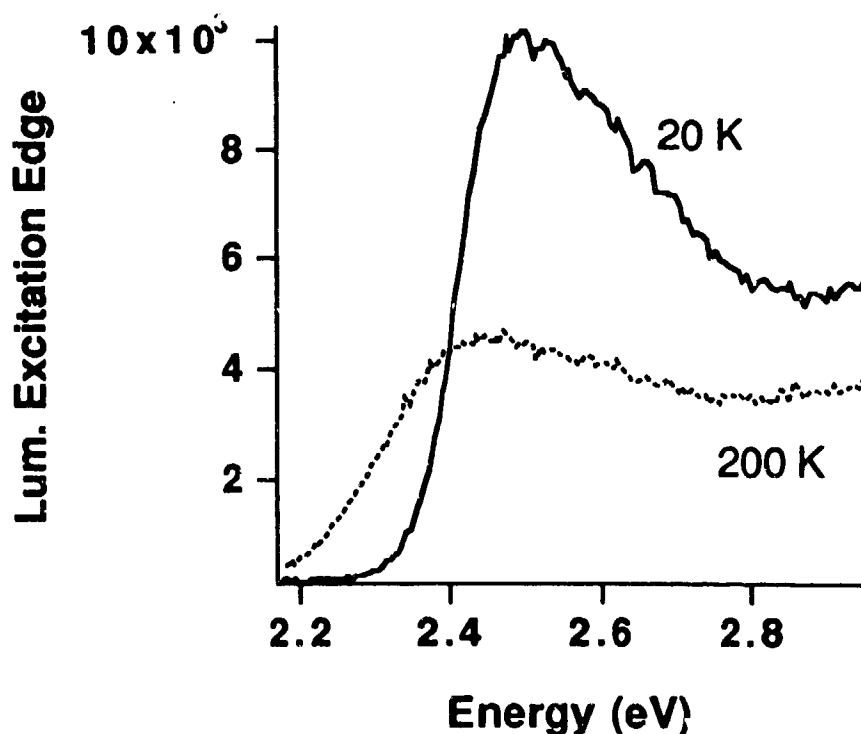
Fig. 1: Excitation Spectra at 10K (solid) and 200K (dots) for PtCl. A low energy tail is clearly observed, even at low temperature. As the temperature is raised, the band edge broadens significantly.

To determine to what extent structural inhomogeneities could be present in our crystals, we have performed RR measurements with excitation energies throughout the band gap and band tail region, from 1.96 eV to 2.71 eV, carefully monitoring the V_1 frequency as a function of excitation energy. As mentioned above, the symmetric halide stretching mode, V_1 is a quantitative measure of the CDW strength, and is directly correlated with the gap energy.[16] This monotonic correlation is expected for a Peierls distorted system.[21] Therefore any kind of static structural disorder (strains, vacancies, interstials, etc.) coupled to the CDW would be manifested by shifts in the V_1 frequency as the Raman excitation comes into resonance with various local environments as it is tuned through the band edge region. We have performed this experiment on a variety of PtCl samples, at temperatures from 15K to 300K, on two separate spectrometers, both with natural Cl isotopic abundance and with isotopically pure ^{35}Cl, and no measurable excitation energy dependence was found. [9,17, 20][a] Thus it is clear that static structural disorder has no significant effect on the electronic or vibrational spectra of our samples. These results are in dramatic contrast to the RR of PA.[5]

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[a]   Early studies by Kurita et al. and Clark et al. did show a dependence of the v_1 freqency on excitation energy, which would be consistent with poor quality crystals with large inhomogeneities.

We believe that lattice fluctuations are the origin of the tail states seen in our luminescence experiments. Because of the lack of structural disorder, MX solids provide a good testing ground for the theory of McKenzie and Wilkins. They predict that as the temperature is increased the density of states in the gap will increase and will produce a large broadening in the absorption band edge. This is totally consistent with what we see experimentally. Furthermore, McKenzie and Wilkins note that these band tail states should be localized. A detailed comparison with the theory of McKenzie and Wilkins will be presented in a future paper.[20]

The effective disorder caused by zero-point lattice fluctuations is distinguished from ordinary static disorder in that only the electronic states are modulated by zero-point lattice motion. The vibrational transition energies are perfectly defined. This is consistent with the previously discussed Raman spectroscopy. Electronic spectroscopy is sensitive to zero-point motion effects because vertical transitions occur on much faster time scales and are therefore sensitive to modulations of the band gap due to bondlength disorder.

The excitation dependence of the luminescence also supports the existence of localized tail states below the band edge. At low temperatures, the luminescence from excitation into the tail of the PtCl band gap is clearly red shifted with respect to luminescence that originates from excitation into the band gap or above, Fig. 2. At temperatures above 200 K, the excitation energy dependence of the luminescence emission profile disappears, data not shown. At higher temperatures, the excitation dependence disappears because the relaxation rate from the band to the localized tail states increases sufficiently so that all luminescence originates from the lowest lying excited electronic states. Previously, a small excitation dependence of the luminescence from PtCl was described in terms of a series Wannier excitons.[15] We have found no excitation dependence of the luminescence in the IVCT region, and these experiments did not examine the luminescence from the band tail states.

Physically the zero-point lattice fluctuations induce a series of localized electronic states below the band edge. The observed excitation dependence of the luminescence suggests that the photo-excitation dynamics of these systems involve non-adiabatic transitions between the band and the localized tail states. Typically theoretical modeling of the photoexcitation dynamics for low dimensional systems has included only the adiabatic relaxation of the lattice around the initially produced electron-hole pair or charge-transfer exciton. Our experiments indicate that non-adiabatic transitions must be included in the simulations of the excited state dynamics in low dimensional CDW solids.[7] Time-resolved spectroscopy should yield important information about these relaxation processes.
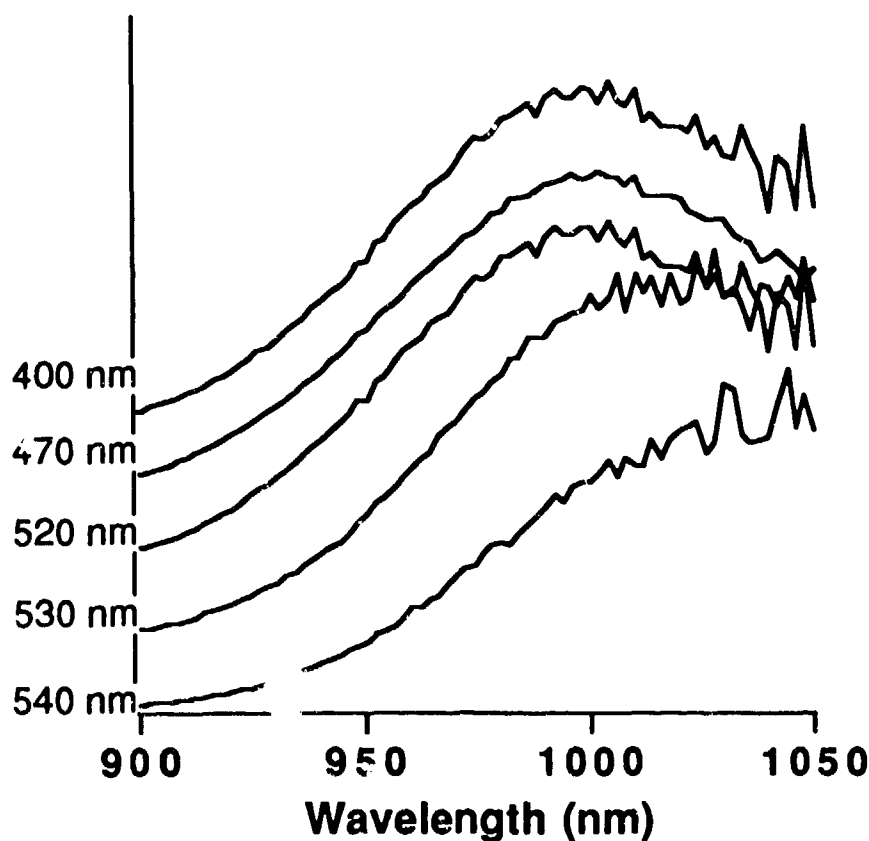
400 nm
470 nm
520 nm
530 nm
540 nm

900 **950** **1000** **1050**

Wavelength (nm)

Fig. 2: Excitation dependence of the PtCl luminescence at 20 K. When the band tail states are excited, the luminescence is strongly red shifted.

4. SUMMARY

The experimental results reported here support the existence of band tail states, reminiscent of the Urbach edge seen in semiconductors, for a 1-D CDW material. Resonance Raman experiments rule out the possibility that structural inhomogeneities are the origin of the band tails. We believe the tail states are due to "disorder" originating from quantum fluctuations of the lattice and the associated modulation of the Peierls energy gap, as predicted by McKenzie and Wilkins.[2]

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